PRODUCTION OF BIODIESEL FROM JATROPHA OIL USING PHASE BOUNDARY CATALYST

MOHD IKHWAN BIN MOHD RASID

A thesis submitted in fulfillment for the award of the degree of Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical and Natural Resources Engineering
University Malaysia Pahang

NOVEMBER 2010

ABSTRACT

Biodiesel is an alkyl ester from reactions of fatty acids with short chain alcohols made by the transesterification of oils or fats from either plants or animals sources in the presence of a catalyst. The objective of this project is to give elemental insight into the transesterification of triglycerides on heterogeneous phase boundary catalyst. In an effort to identify catalyst characteristics that would be ideal for biodiesel synthesis, this study present the result from BET Surface Area analysis, Hydrophobic-Hydrophilic test, Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD) analysis, Scanning Electron Microscopy (SEM) analysis, Transmission Electron Microscopy (TEM) analysis and catalytic activity of heterogeneous phase boundary base catalysts with different hydrophobicity in the transesterification of jatropha oil. The potassium fluoride (KF) anchored on solid material is believed to be capable in catalyzing the transesterification of triglycerides, but this reaction is favorable with the catalyst that possesses hydrophobic environment for the triglycerides to adsorb on the base sites to produce the fatty acid methyl esters. In this research, four types of catalysts were prepared. The first design was calcined zirconium. The second catalyst is with full coverage of potassium fluoride (KF) attached on the zirconia surface creating base sites. This catalyst is believed to be less hydrophilic than the first design. The third catalyst designed was prepared by partially attachment of octadecyltrichlorosilane (OTS) and KF while the fourth catalyst was modified by partially attachment of the chlorotrimethylsilane (CTMS) and KF onto the zirconia surface. The purpose of using OTS and CTMS are to create hydrophobic environment around the catalyst and to determine the enhancement of hydrophobic groups to the reaction. The catalytic results suggest that the third design catalysts perform very well with catalyst dosage of 5 wt% at 65 ºC, ratio of methanol and jatropha oil at 9:1 with 8 hours reaction time, yield 85 % conversion of methyl ester.

ABSTRAK

Biodiesel merupakan ester alkil dari reaksi asid lemak dengan alkohol rantai pendek yang dibuat oleh tindakbalas pengtransesteran minyak atau lemak, baik dari sumber tumbuhan atau binatang dengan kehadiran mangkin. Objektif projek ini adalah untuk memberikan pendedahan mendalam berkaitan pengtransesteran trigliserida menggunakan mangkin heterogen sempadan pemisah fasa. Dalam usaha untuk mengenalpasti ciri-ciri mangkin yang akan ideal untuk sintesis biodiesel, kajian ini membentangkan hasil dari analisis BET Surface Area, ujian hidrofobik-hidrofilik, analisis Termogravimetri (TGA), X-Ray Diffraction (XRD), analisis Scanning Elektron Mikroskop (SEM), analisis Mikroskop Elektron Transmisi (TEM) dan aktiviti katalitik mangkin heterogen sempadan pemisah fasa dengan permukaan hidrofobik berbeza dalam pengtransesteran minyak jatropha. Kalium fluorida (KF) membuat ikatan pada bahan padat dipercayai mampu mengkatalisis pengtransesteran trigliserida, tetapi tindakbalas ini adalah lebih baik dengan kehadiran mangkin yang mempunyai persekitaran hidrofobik untuk trigliserida untuk menyerap pada struktur bes untuk menghasilkan metil ester asid lemak . Dalam kajian ini, empat jenis mangkin dihasilkan. Rekaan pertama adalah zirkonium yang dikalsinasi. Mangkin kedua dengan liputan penuh kalium fluorida (KF) melekat pada permukaan zirkonia menghasilkan sruktur bes. Mangkin ini dipercayai kurang hidrofilik dari rekaan pertama. Mangkin ketiga direka dengan sebahagian ikatan octadecyltrichlorosilane (OTS) dan KF sedangkan mangkin keempat direka dengan sebahagian ikatan chlorotrimethylsilane (CTMS) dan KF ke permukaan zirkonia. Tujuan menggunakan OTS dan CTMS adalah untuk mencipta persekitaran hidrofobik sekitar mangkin dan meningkatkann kebolehan kumpulan hidrofobik untuk tindakbalas. Keputusan katalitik menunjukkan bahawa rekaan ketiga mangkin menunjukkan prestasi yang terbaik dengan dosis mangkin 5 % wt pada suhu 65 ºC, nisbah metanol dan minyak jatropha adalah 9:1 dan 8 jam waktu tindakbalas, menghasilkan 85 % metil ester dari minyak jatropha.

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LIST OF ABBREVIATIONS

$AgNO_3$	-	Silver Nitrate
BET	-	Brunauer – Emmett – Teller
CO_2	-	Carbon Dioxide
CTMS	-	Chlorotrimethylsilane
EPA	-	Environmental Protection Agency
FAEE	-	Fatty Acid Ethyl Esters
FAME	-	Fatty Acid Methyl Esters
FFA	-	Free Fatty Acids
FID	-	Flame Ionization Detector
FTIR	-	Fourier Transformed Infrared Spectroscopy
GC	-	Gas Chromatography
$HZSO_4$	-	Sulfuric Acid
IFF	-	French Institute of Petroleum
KF	-	Potassium Fluoride
KOH	-	Potassium Hydroxide
MCM	-	Mobil Composition of Matter
NaOH	-	Sodium Hydroxide
OTS	-	Octadecyltrichlorosilane
SEM	-	Scanning Electron Microscope
TEM	-	Transmission Electron Microscopy
TGA	-	Thermogravimetric Analysis
TG/DTA	-	Thermogravimetric/Differential Thermal Analysis
w/w%	-	Weight Over Weight Percentage
XRD	-	X-Ray Diffraction
$ZrOCl_2.8H_2O$	-	Zirconium Oxychloride

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Diesel fuels have an essential function in the industrial economy of a developing country and used for transport of industrial and agricultural goods and operation of diesel tractor and pump sets in several industrial sectors (Meher *et al.*, 2006). Scarcity increased prices and have a significant impact on world economies whereas combustion of oil and oil-based products such as petrol produces greenhouse gases that are responsible for global warming. Global warming also has significant impacts on global economies, societies and the environment. For these reasons, alternatives to fossil oil and derived products are sought.

Biodiesel is a renewable alternative to petroleum diesel and receive tremendous attention worldwide. The usage of biodiesel reduces emissions of hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, and particulate matter. Besides, it is less toxic and biodegrades more rapidly compared to petroleum diesel (Singh *et al.*, 2008). Basically, biodiesel is produced through transesterification of triglycerides in the oils and fats feedstock like vegetable or animal with an alcohol and the presence of a catalyst which results in the formation of alkyl esters.

Several feedstocks from vegetable source such as soybean oil, rape seed oil, canola oil, palm oil, corn oil and Jatropha oil have been studied as a biodiesel candidate. Among these sources, Jatropha oil is a potentially promising feedstock since it has higher composition of triglycerides compared to the others. Jatropha oil contains of several fatty acids. Some studies shows that oleic acid is the most abundant (44.8 %) followed by linoleic acid (34 %), palmitic acid (12.8 %), and stearic acid (7.3 %) (Shah *et al.*, 2004).

There is two-step method to convert raw Jatropha oil into biodiesel. A pre-esterification operation was applied to eliminate free fatty acids (FFA) by reacting the oil with methanol in the presence of an acid catalyst. The process can be simply described as pre-esterification then purification followed by transesterification and end with phase separation. Raw Jatropha oil was firstly reacted with methanol, followed by phase separation to remove acidic water and gum impurities. The purified oil was further reacted with methanol in the presence of an alkali catalyst. Finally, the biodiesel product was separated from the glycerol by-product by phase separation. In this work, factors influencing the pre-esterification and transesterification were systematically investigated (Lu *et al.*, 2008).

1.2 Identification of Problem

Currently, most of biodiesel oil is produced by the alkaline process with overall world production was about 8.5 millions of tones in 2007 (Licht F.O World Ethanol & Biofuels Report, 2008). Current method for production of biodiesel uses alkaline catalysts because the transesterification reaction is much faster as compared to acid-catalyzed reaction (Srivastava *et al.*, 2000). The homogeneous alkaline-catalyzed transesterification reaction usually uses sodium hydroxide (KOH) as the catalyst (Pen *et al.*, 2009). Generally, basic catalysts yield higher conversion rates from triglycerides to methyl esters especially if the acidity index is higher than 0.5 %. The alkaline catalysts show high yield of biodiesel with high quality, but causes a problem when the oils contain significant amounts of free fatty acids. The free fatty acids cannot be converted into biodiesels but will be converted to large amount of soap in the presence of sodium or potassium ions, thus making separation of the glycerin from the methyl ester more difficult (Furuta *et al.*, 2004 and Di Serio *et al.*, 2005).

Homogeneous acid-catalyzed processes could produce biodiesel from low-cost feedstock, thus lowering production costs (Fukuda *et al.*, 2001). However, the homogeneous acids such as hydrochloric acid and sulfuric acid require longer reaction time as compared to the alkaline catalysis (Lotero *et al.*, 2005 and Meneghetti *et al.*, 2006). Based on the drawbacks from homogeneous-catalyzed acid and base reactions, we are proposing a new design of heterogeneous solid-base catalyst for biodiesel transesterification process since heterogeneous catalysts offer several intrinsic advantages over their homogeneous counterparts: including ease of product separation and catalyst recyclability. Amphiphilic high surface area zirconia impregnated with base are design to catalyze the two immiscible reaction mixtures and enable the transesterification reaction to occur at specific temperature with ambient pressure in a short reaction time.

1.3 Statement of Objectives

The main objectives of this study are to synthesis phase boundary catalyst by using zirconia and to produce biodiesel via transesterification reaction with zirconia as catalyst at different reaction time, different oil and solvent ratio and via adiabatic process.

1.4 Research Scopes

The research scopes for this study are:

i. To produce hydrophobic and hydrophilic phase boundary catalyst from zirconia with high surface area.
ii. To perform characterization of catalyst to determine existence of hydrophobic and hydrophilic site on the catalyst produced.
iii. To produce biodiesel using the catalyst produced at different reaction time and different oil and solvent ratio.
iv. To study effect of adiabatic process in the transesterification reaction with phase boundary catalyst produced at fixed reaction time and oil to solvent ratio.

1.5 Rationale and Significances of Study

Due to gradual depletion of world petroleum reserves and the impact of environmental pollution of increasing exhaust emissions, there is an urgent need for suitable alternative fuels for use in diesel engines. In view of this, vegetable oil is a promising alternative due to several advantages, such as renewable, environmental friendly and can be produced easily in rural areas, where there is an acute need for modern forms of energy. The used of Jatropha biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter compared to emission from diesel fuel. In addition, the exhaust emissions of sulphur oxides and sulphates from Jatropha biodiesel are essentially eliminated compared to diesel. The uses of Jatropha biodiesel result in substantial reduction of unburned hydrocarbons. Emission of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Based on engine testing, using the straightest emissions testing protocols required by Environmental Protection Agency (EPA) for certification of fuels or fuel additives in the United States, the overall ozone forming potential of the specificity hydrocarbon emission from Jatropha biodiesel was nearly 50 percent less than that measured for diesel fuel (Busari, 2005).

The cost of biodiesel could certainly be lowered by the using of heterogeneous catalyst instead of a homogeneous one, resulting in a higher quality of esters and glycerol, which can be more easily and promptly separated. Glycerol is by-product of reaction and its refining operations cost were expensive. Latest news announced in France was the construction of a new 160 000 tone/year biodiesel plant based on the use of heterogeneous catalyst developed by the French Institute of Petroleum (IFF). Many other heterogeneous catalysts, characterized by both acid and basic catalytic sites, have recently been proposed in the literature, but only a little information has been provided about the influence of the amount of FFA on the reaction. On the other hand, it is evident from all the published papers that to pass from the current technology based on the use of homogeneous alkaline catalysis to a new approach based on the use of heterogeneous catalysts is a fundamental goal for lower-cost biodiesel production (Di Serio *et al.*, 2007).

1.6 Design of Catalyst

Heterogeneous catalysts offer several intrinsic advantages over their homogeneous counterparts: ease of product separation and catalyst reuse; bifunctional phenomena involving reactant operation in continuous flow versus batch configuration. However, a suitable heterogeneous system must not only minimize the production of waste, but should also exhibit activities and selectivity comparable or superior to the existing homogeneous route.

Figure 1.1 shows the synthesis route in designing amphiphilic catalyst from zirconia with Potassium Fluoride (KF) for hydrophilic site while Octadecyltrichlorosilane (OTS) and Chlorotrimethylsilane (CTMS) with alkyl chain cover the hydrophobic site of the catalyst. KF work as compound that attract polar substances in the reaction which in transesterification reaction, glycerol is the polar substance exist as by product of the reaction. Meanwhile OTS and CTMS help in bonding the non-polar substances in one reaction with the core catalyst and speed up the catalytic performances of the prepared catalyst.

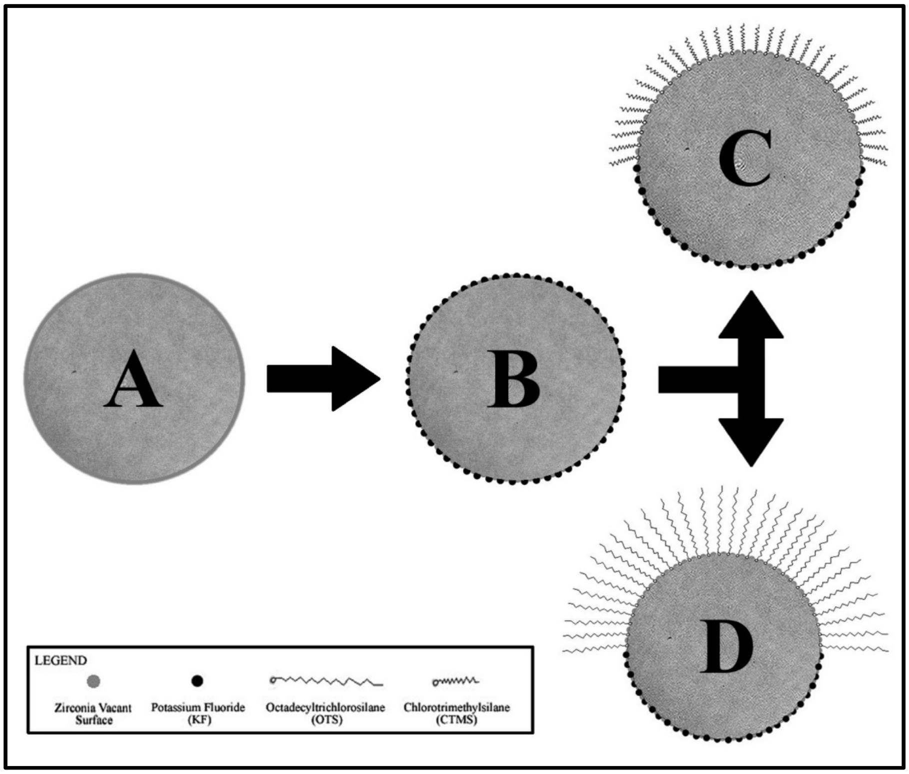

Figure 1.1: Proposed model of (A) ZrO_2, (B) 4KF/ZrO_2, (C) CTMS-4KF/ZrO_2 and (D) OTS-4KF/ZrO_2

Basically, zirconia are calcined to remove moisture and water contain in the zirconia framework then followed by two different procedures, the modification of zirconia with KF to synthesis 4KF/ZrO_2 and the one-step impregnation of base zirconia containing KF with OTS and CTMS to synthesis OTS-4KF/ZrO_2 and CTMS-4KF/ZrO_2. The impregnation method is currently the most common and direct route to the introduction of the organic groups into the zirconia framework. It provides better control over the amount of organic groups incorporated into the matrix and ensures the uniform surface coverage with organic groups under mild conditions (Afanasieva *et al.*, 2007). Generally, the direct synthesis procedures usually lead to higher content of functional groups (Joaquín *et al.*, 2007).

In the grafting method, the original structure of the zirconia is usually maintained after the modification. Silylation reagents were also typically added under dry conditions to avoid hydrolysis and condensation away from the surface (Qiu *et al.*, 2007). The reaction that we expect to occur on the zirconia surface is shown in Figure 1.2. It is proposed that this solid acid catalyst with higher hydrophobicity could catalyze the transesterification with high reaction rate producing methyl esters yield without occurring of reverse reaction.

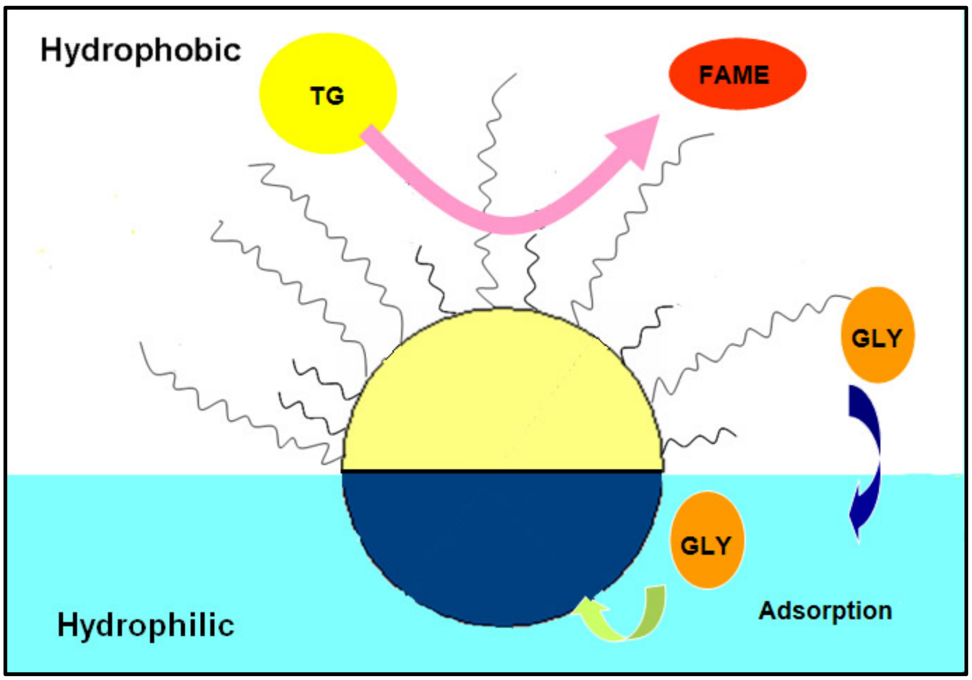

Figure 1.2: Proposed model of the catalytic system

CHAPTER 2

LITERATURE REVIEW

2.1 Basic Concept of Biodiesel

Depletion of the world petroleum reserves and increasing environmental concerns has stimulated the search for renewable fuels, such as biodiesel, in recent years. Because the production demand gap of fossil fuel is fluctuating worldwide, the risk in energy supply security increases, the price of conventional fossil fuel continues to rise, and the economies of importing nations suffer significant disruption. From an environmental perspective, combustion of petroleum fuels is a main contributor of an increasing global carbon dioxide (CO_2) atmospheric concentration, a driver of global warming. These concerns have driven significant investment into alternative energy sources for internal combustion engines (Li *et al.*, 2007). Biodiesel is the name of clean burning alternative fuel, produced from domestic, renewable resources such as Jatropha seeds, recycled restaurant greases, and animal fats. Biodiesel contains no petroleum, but it can be blended at any level with petroleum diesel to create a biodiesel blend. It can be used in compression-ignition also known as diesel engines with little or no modification. Biodiesel is simple to use biodegradable, nontoxic and essentially free of sulphur and aromatics. Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the 1990 clean Air Act Amendments (Busari, 2005).

2.1.1 Conventional Production Methods

The direct use of vegetable oils as biodiesel is possible only by blending them with conventional diesel fuel in a suitable ratio, but the direct usage of vegetable oils in diesel engines is not technically possible because of their high viscosity, low stability against oxidation and low volatility, which influence on the formation of a relatively high amount of ashes due to incomplete combustion. Therefore, vegetable oils must be processed so as to acquire the properties necessary to be directly used in current diesel engines. The possible processes are pyrolysis or cracking, microemulsion and transesterification (Hanna *et al.*, 1999). As the first two are cost intensive processes, yielding a low quality biodiesel, the most usual method to transform oil into biodiesel is transesterification. This consists of the reaction between triacylglycerols that contained in the oils and an acyl-acceptor. The acyl group acceptors may be carboxylic acids, alcohols or another ester. Only alcohols and interesterification are of interest to produce biodiesel. The starting esters in both are triacylglycerols in oils and if the transformation is quantitative they yield a mixture of monoalkyl esters also known as biodiesel and glycerol or excessive triacylglycerol.

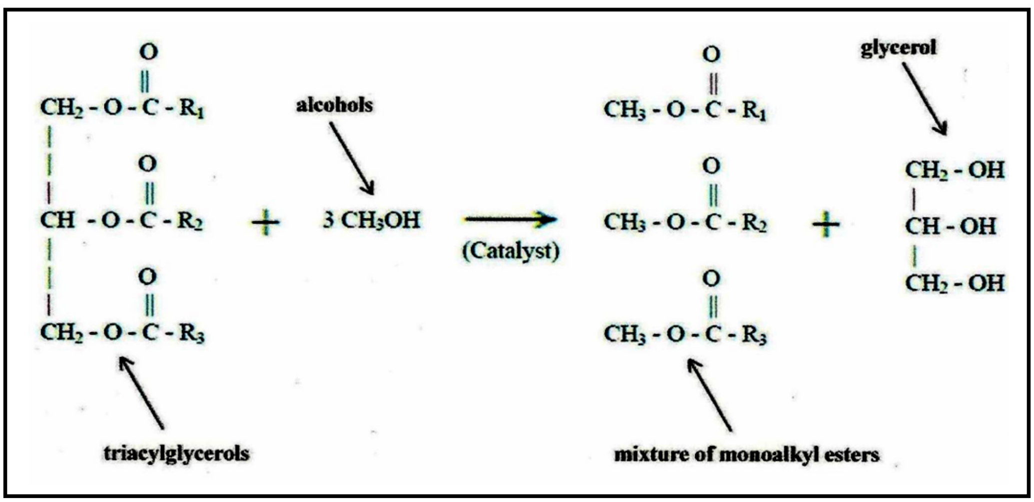

Figure 2.1: Transesterification reaction

Alcohols are the most frequently used acyl-acceptors, particularly methanol and, to a lesser extent, ethanol. Other alcohols can be used such as propanol, butanol, isopropanol, tert-butanol, branched alcohols and octanol but the cost is much higher. Regarding the choice between methanol and ethanol, the former is cheaper, more reactive and the fatty acid methyl esters (FAME) are more volatile than those of the fatty acid ethyl esters (FAEE). However, ethanol is less toxic and it can be considered more renewable because it can be easily produced from renewable sources by fermentation. In contrast, methanol is mainly produced from non-renewable fossil sources, such as natural gas. Regarding their characteristics as fuels, FAME and FAEE show slight differences; for example, FAEE have slightly higher viscosities and slightly lower cloud and pour points than the corresponding FAME (Bozbas, 2008).

2.1.2 Free Fatty Acid

Commonly, biodiesel is prepared from triglycerides sources such as vegetable oils, animal fats, and waste greases such as yellow and brown greases. Oils and fats belong to an ample family of chemicals called lipids. In general, lipids are found in animals and plants. Typically, fats come from an animal source and oils from a plant source. Fats and oils are primarily formed of triglycerides molecules. A triglycerides molecule is basically a triester of glycerol and three fatty acids with long alkyl chain carboxylic acids (Lotero *et al.*, 2005). Due to economic and environmental issue, the main raw materials used to produce biodiesel are the vegetable oils extracted from oleaginous plants. The cost of these materials currently represents about 70 % of the total production costs (Behzadi *et al.*, 2008). It is extremely important to realize that vegetable oils are mixtures of triglycerides from various fatty acids. The composition of vegetable oils varies with the plant source. Often the terms fatty acid profile or fatty acid composition are used to describe the specific nature of fatty acids occurring in fats and oils (Gerpen *et al.*, 2004).

Fats and oils may be characterized according to their physical such as density, viscosity, melting point, refractive index, or chemical properties such as acidity, iodine index, peroxide index, saponification index. These parameters will influence on the biodiesel quality. For example, the iodine index is related to the grade of oil unsaturation and in general, biodiesel produced from high unsaturated fatty acids containing oils are less viscous, show greater cloud point, the temperature at which fuel becomes cloudy due to solidification and pour points, temperature at which fuel stops flowing which make this biodiesel more suitable for cold weather conditions. However, it is also prone to oxidation, has a lower cetane index which related to reaction efficiency within the engine and lower combustion heats. In contrast, the biodiesel produced from oils with a high proportion in long chain fatty acids have a higher cetane index and combustion heat, but also lower cloud and pour points and greater viscosity (Knothe, 2005). Figure 2.2 shows the fatty acid profile of some of the raw materials used in biodiesel production.

Oil	$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$	$C_{20:1}$	Others	Ratio SFA[a]/UFA[b]
Almond	6.5	0.5	1.4	70.7	20.0				0.9	7.9/91.2
Borage	12.9	0.2	4.3	19.1	39.0	18.7	0.3	3.5	2.0	17.5/82.5
Corn	11.7		1.9	25.2	60.5	0.5	0.2			13.8/86.2
Cotton seed	28.3		0.9	13.3	57.5					29.2/70.8
Jatropha	16.4	1.0	6.2	37.0	39.2		0.2			22.8/77.2
Olive	11.8	1.5	2.7	74.1	8.5	0.7	0.4	0.3		14.9/85.1
Palm	42.6	0.3	4.4	40.5	10.1	0.2			1.9	47/51.1
Canola	3.5		0.9	64.4	22.3	8.2			0.7	4.4/94.9
Soybean	11.4		4.4	20.8	53.8	9.3	0.3			16.1/83.9
Sunflower	7.1		4.7	25.5	62.4		0.3			12.1/87.9

[a] SFA: sum of saturated fatty acids.
[b] UFA: sum of unsaturated fatty acids.

Figure 2.2: Fatty acid profile (% moles) of vegetable oils used for biodiesel productions (Akoh *et al.*, 2007)

2.2 Features of Jatropha

Jatropha tree as shown in Figure 2.3 is a small trees or shrub with smooth gray bark, which exudes whitish colored, watery, latex when cut. Normally, it grows between three and five meters in height, but can attain a height of up to eight or ten meters under favorable conditions. It has large green to pale-green leaves, alternate to sub-opposite, three to five lobed with a spiral phyllotaxis. The petiole length ranges between 6-23 mm. Flowers are formed terminally, individually, with female flowers usually slightly larger and occur in the hot seasons. In conditions where continuous growth occurs, an unbalance of pistillate or staminate flower production results in a higher number of female flowers. More number of female flowers is grown by the plant if bee keeping is done along with and give more number of seeds. Fruits are produced when the shrub is leafless, or it may produce several crops during the year if soil moisture is good and temperatures are sufficiently high. Each inflorescence yields a bunch of approximately 10 or more ovoid fruits. The seeds become mature when the capsule changes from green to yellow, after two to four months from fertilization. The blackish, thin shelled seeds are oblong and resemble small castor seeds.

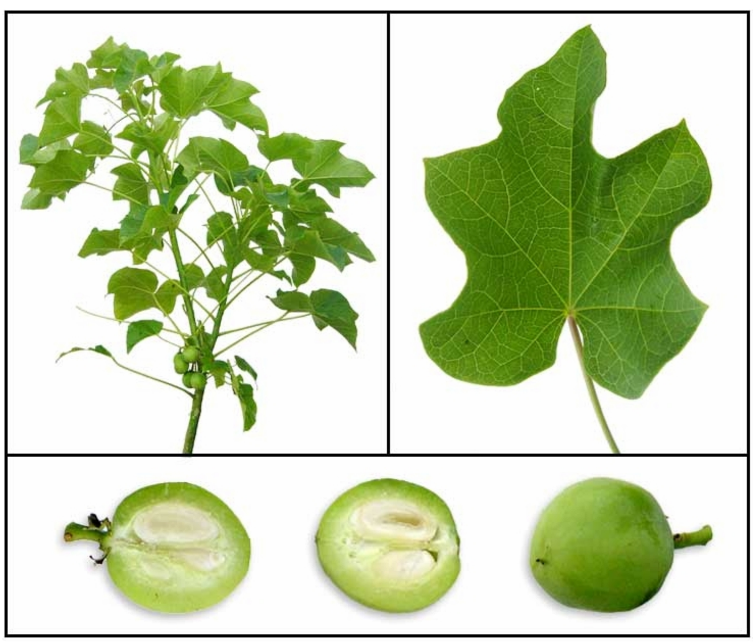

Figure 2.3: Jatropha tree, leaves and fruits

2.2.1 Jatropha Oil as Alternative Fuel

Recently, Jatropha curcas oil, a non-edible vegetable oil which has been considered as a potential alternative fuel for compressed engines. Jatropha curcas is a large shrub or tree native to the American tropics but commonly found and utilized throughout most of the tropical and subtropical regions of the world. Several properties of the plant, including its hardness, rapid growth, easy propagation and wide ranging usefulness have resulted in its spread far beyond its original distribution. The Jatropha oil is slow-drying oil which is odorless and colorless when fresh but becomes yellow on standing. The oil content of Jatropha seed ranges from 30 to 50 % by weight and the kernel itself ranges from 45 to 60 %. The fatty acid composition of Jatropha is classified as linoleic or oleic acid type, which are unsaturated fatty acids. The fatty acid composition of Jatropha oil consists of myristic, palmitic, stearic, arachidic, oleic and linoleic acids. The seeds and oil are toxic due to the presence of cursive and curcasive. However, from the properties of this oil it is envisaged that the oil would be suitable as fuel oil. The oil compares well against other vegetable oils and more importantly to diesel itself in terms of its fuel rating per kilogram or hectare of oil produced (Pramanik, 2002).

2.2.2 Environmental and Economical Analysis on Jatropha Oil

Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the Clean Air Act. The used Jatropha biodiesel in a conventional diesel engine results in substantial reduction of unburned hydrocarbons, carbon monoxide, and particulate matter compared to emission from diesel fuel. In addition, the exhaust emissions of sulphur oxides and sulphates, one of major component of acid rain, from Jatropha biodiesel are essentially eliminated compared to diesel. The use of Jatropha biodiesel results in substantial reduction of unburned hydrocarbons. Emission of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Based on engine testing, using the straightest emissions testing protocols